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Sustainable solar energy conversion to chemical and electrical energy

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ABSTRACT

The Earth receives around 1.9×10^6 EJ of energy in visible light each year and only a fraction of this light energy is being converted to biomass (chemical energy) via the process of photosynthesis. Out of all photosynthetic organisms, microalgae, due to their fast growth rates, have been identified as potential source of raw material for chemical energy production. Solar panels have also been used worldwide for electrical energy production. Here we explore and introduce a novel methodology on combining solar panels with microalgae cultivation systems. These two methods of energy production would appear to compete for use of the same energy resource (sunlight) to produce either chemical or electrical energy. However, some groups of microalgae (i.e. Chlorophyta) only require the blue and red portions of the spectrum whereas certain types of solar cells absorb strongly in the green part of the solar spectrum but not as much in the red or blue portion of the spectrum. This suggests that a combination of the two energy production systems would allow for a full utilisation of the solar spectrum allowing both the production of chemical and electrical energy from one facility making efficient use of available land and solar energy. In this review we propose to introduce a solar panel as a filter above the algae culture to modify the spectrum of light received by the algae and utilise the unused parts of the spectrum to generate electricity.

Contents

1. Introduction

The global final annual primary consumption in 2010 was estimate to be 3.44×10^{17} Btu [1]. A very small amount of this primary energy was derived from non-fossil fuel resources. Furthermore, the

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estimated world fossil fuel reserve depletion times for oil, coal and gas is 2044, 2116 and 2046 respectively [2]. This means that in the post year 2046 there will be almost no liquid fuel available for transport. In relation to liquid fuels, between January 1990 and 2012 a barrel of North sea crude oil fluctuated between US$20 and US$90, which at present seems to have stabilised at around US$90 (all in 2012 dollar terms) [1]. Furthermore, the energy information administration (EIA) has projected that world energy consumption will increase at an average rate of 1.1% y^{-1} from 5.05×10^{17} Btu to 7.70×10^{17} Btu between 2008 and 2035 [3]. Therefore, the decline of finite fossil fuel resources, as well as recognition of global warming together with an ever increasing global demand for energy has led to substantial interest and activity in developing alternative renewable fuels.

One of these alternative renewable energy supplies can be generated directly from sunlight by using photovoltaic modules (solar panels). This has been described as the 'art of converting sunlight directly into electricity' [4]. Photovoltaic devices, or solar cells, are capable of using incident illumination to supply electrons to an external circuit. Although the first few solar cells were used primarily in the space programme, there has been an increasing demand for terrestrial applications and we are now seeing widespread adoption of photovoltaic roof top arrays.

Biomass has been used widely for millennia as a source of chemical energy. Modern commercial liquid biofuels are bioethanol and biodiesel. Bioethanol is mostly produced from fermenting sugarcane and, biodiesel is made through the process of transesterification of vegetable oil [5]. It is projected that the global annual production of bioethanol and biodiesel will increase from 75×10^9 and 15×10^9 L in 2007 to 159×10^9 and 41×10^9 L in 2019, respectively [6]. The production of renewable transport fuels from crops such as oilseeds or sugarcane has economic as well as ethical problems, and it is mainly due to the potential competition for limited resources with food crops. Therefore, there is a need for an alternative source of raw material for chemical energy (i.e. biomass) production.

Microalgae are microscopic plant-like largely photosynthetic organisms belonging to a number of Phyla (major taxonomic groups) [7]. They are extremely diverse and can be found in most habitats of the world including fresh and sea water, salt lakes, soil, snow and on surfaces such as rocks and the bark of trees [7]. The size of algae ranges from about 1 μm (nanoplanktons) to more than 40 m (kelp). Microalgae have been suggested as a raw material for bioethanol and biodiesel production [8,9] and since a United Nations committee recommended that conventional agriculture be supplemented with high-protein foods of unconventional origin, microalgae have become natural candidates for this [10]. Without any doubt, the primary source of all food and organic raw materials is solar energy [11–13]. Exponential increases in the world's population and its demands for finding possible resources of food and energy will depend on how efficiently we can learn to use solar energy. Conventional agricultural systems are very inefficient in this respect as (1) most plants can only utilise less than 0.5% of the sun light that falls on them, (2) most farms cover only a small land area, (3) only a small proportion of each crop plant is edible, and (4) maximal production is highly limited by the availability of CO_2 [11].

2. Microalgae

Microalgae promise important advantages to improve the solar efficiency utilisation that (1) they can be grown reliably long term in semi-continuous and continuous culture providing maximal annual productivity, (2) microalgal cells contain relatively low structural material with the possibility of using the whole biomass for nutrition or other economic uses, and (3) addition of CO_2 to a microalgal culture systems is relatively simple compared to field crops [14–18]. Despite all of these advantages of microalgae over conventional agriculture, the feasibility of microalgae as a food or fuel source is yet to be proven and it is mainly limited by the high cost of production [9]. Production of microalgae is, on the other hand, already an economical method of aquaculture feed and high value products [17,19,20]. Decreasing the cost of microalgae production for different purposes such as a source of oils, polysaccharides, fine chemicals, etc. has been the subject of many studies since 1940s [21]. During the 1950s a world-wide interest in novel sources of protein to feed the growing human population led researchers to investigate the possibilities of large-scale algal cultivation systems [21]. The use of microalgae as a source of biofuel offers an attractive sustainable alternative to other raw materials as algae production does not necessarily compete for fresh water (e.g. marine algae) or arable land [9]. Furthermore, algae photosynthetic rates are higher on an areal basis than terrestrial plants and this offers an accordingly smaller footprint of the operation, provided a suitable climate and sunshine hours are available (e.g. Western Australia). For instance, the Pacific Northwest National Laboratory, part of the U.S. Department of Energy, reported that renewable fuel from algae alone could eventually replace 17% of U.S. oil imports [22]. While microalgae seems to be a very important contender for biofuel production, to date and despite a large investments in this field, no large scale economical microalgae fuel has been made. One of the main reasons for the lack of success in this field is factors limiting growth of microalgae.

Microorganisms, especially bacteria, have been successfully cultured in large-scale systems such as fermenters for more than half a century. The basic principles of microalgal cultures are the same as other microbial cultures with the exception of the light requirement in autotrophic or mixotrophic cultures. For successful microalgal culture, a suitable species must be selected mainly based on general physical chemical and biological characteristics together with the growth optimisation of selected species on a suitable medium [14].

The question of what limits algal growth and product yield in microalgal cultures is of fundamental importance in the development of a commercial large-scale algal process. High cell density mass production cultures are unattainable due to a number of physical, chemical and biological factors [23,24]. These factors are: (a) light (quality and quantity), (b) temperature, (c) nutrient concentrations (i.e. N, P, Si, Fe), (d) CO_2, pH, bicarbonate and alkalinity, (e) growth inhibitors, (f) mixing (too much or too little), (g) dilution rate, harvest frequency and pond depth and (h) contaminations by pathogens or other algae.

2.1. Light

The Earth receives around 3.9×10^6 EJ of total solar energy [25], with 48% in visible light, each year and only a fraction of this light energy is being converted to biomass (chemical energy) via process of photosynthesis. Photosynthesis can only use solar spectrum in the range of 400 and 700 nm which is called photosynthetic active radiation (PAR). Based on the measured average solar spectrum at the Earth's surface, the proportion of total solar energy within PAR is about 48.7% of the incident solar energy [26]. The most important limiting factor for the mass cultivation of microalgae, irrespective of the cultivation system, concerns the effective use of light [27]. This is especially important in mass cultivation of microalgae outdoors as growth and performance of all photosynthetic organisms are strongly linked to the quality and quantity of available light [28,29]. The amount of light absorbed by an algal cell suspended in an algal cultivation system depends on many factors, including the specific position of the cell at a given instance, the density of the culture, and the pigmentation of the cells [30] (for more details see section *Light*

Spectrum and Photosynthesis). Therefore, the spectrally averaged optical absorption cross-section normalised to chlorophyll *a* is a key parameter in phytoplankton photophysiology and ecology [31].

Photoinhibition is defined as a light-induced depression of photosynthesis that is (1) manifested as a decrease in the maximum quantum yield of photosynthesis, (2) can decrease photosynthesis light conversion efficiency, and (3) can decrease the rate of light-saturated photosynthesis mainly during prolonged exposure to high irradiance [32,33]. Photoinhibition is also described as a loss of the photosynthetic capacity due to damage caused by high irradiance [24,34]. Outdoor microalgal cultures are exposed to diurnal changes in environmental conditions, especially irradiance and temperature [14]. These environmental factors vary during the day between limiting and possibly inhibiting of photosynthesis [14]. De-synchronization between these two most important environmental factors may induce stress on photosynthesis and the growth of outdoor microalgal cultures [24,35]. In general, light is found to be a major limiting factor of productivity and growth when nutritional requirements are satisfied and the temperature is not far from optimal [24,36]. However, in open outdoor systems such as raceway ponds, light is rarely the only limiting factor for algal growth and production of biomass [10] and predicting culture performance requires an understanding of the relationship between the light observed and photosynthesis [37]. Operative management of large-scale microalgal cultures requires an understanding of factors (i.e. position of cultivation system) such as the light regime of the average cell and the best possible cell density [38]. Therefore, the best practice on how to manage the amount of light received by cells can be based on (a) optimising culture operating depth (i.e. variation of depth in various seasons), and (b) manipulating microalgae cell densities

Growth of many algal species is inhibited by oxygen levels above air saturation [39] and this inhibition can be seen in both closed and open cultivation systems [24,40]. A number of studies have suggested that O_2 and active oxygen species (e.g. O_2^- and $^{\bullet}OH$) can also cause photoinhibition of photosynthesis [41,42]. Furthermore, in cultivation systems, the irradiance/photosynthesis relationship can be summarised as follows: (a) light limited region in which photosynthesis intensifies with increasing irradiance, (b) light-saturated area in which photosynthesis is not dependent on irradiance, and (c) photoinhibited region in which photosynthesis decreases with any further photon flux density [24,43].

2.2. The solar spectrum

Light is electromagnetic radiation received from the Sun. The irradiance from the sun varies widely with wavelength and has been well characterised [44]. The extraterrestrial spectrum varies from the terrestrial spectrum as measured from the Earth′s surface. There are a set of two standard terrestrial solar spectral irradiance distributions [45] used in the testing of photovoltaic modules as they provide a wavelength distribution of the solar irradiance which allows the efficiency and performance of different solar modules to be compared.

One of the standards as described details the irradiance on both a flat surface and a surface tilted 37° to the horizontal, towards the Sun [46]. The first of these is applicable for irradiance upon an arbitrary flat surface while the latter is a reasonable average for photovoltaic panels tilted towards the equator, in the United States of America and regions of Australia. The standard defined in ASTM G-173-03 [45] takes into account average values for the atmospheric composition, aerosols, water vapour and ozone content.

A plot of the extraterrestrial irradiance and the two spectra defined in the ASTM G-173-03 standard is shown in Fig. 1. The irradiance is dependent on the air mass, or path length of irradiation through the atmosphere. The spectra in ASTM G-173-0 use an air mass of 1.5, which is a good average for the

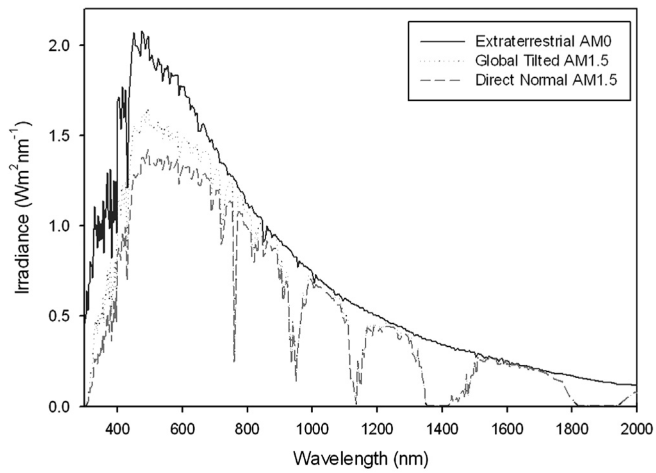

Fig. 1. Solar spectrum as defined in ASTM G-173-03 [45].

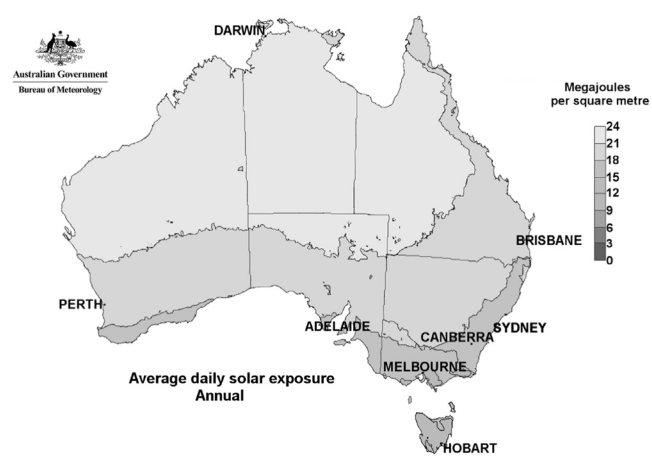

Fig. 2. Average daily solar exposure from Australian Bureau of Meteorology [48].

mid-latitudes. The daily global solar radiation exposure is the total amount of solar energy falling on a horizontal surface per day. These values typically range from 1 to 35 MJ m^{-2}. For mid-latitudes, the values are usually highest in clear sun conditions during the summer and lowest during winter or very cloudy days. There are certain parts of the world which have higher rates of solar exposures. For instance, the northern portion of Australia is particularly suited to activities that require large amounts of incident illumination [47]. The annual average daily solar exposure for Australia shows the amount of solar energy falling on a horizontal surface [48]. This varies from region to region due to seasonal variations, the distance from the equator and regional cloud cover (Fig. 2). The northern and central regions of Australia are particularly good for photovoltaic electricity production and biomass production due to the large amounts of incident illumination [47,49]. Some of these regions, where abundant water supplies (i.e. seawater or large aquifer resource) are available can especially be prime locations for algae farms and biofuel production [47]. These are often in remote areas that require remote area power supplies for which photovoltaics are one solution. Blending these two activities could reduce capital costs.

2.3. Light spectrum and photosynthesis

Compared to most higher plants, microalgae lives in habitats with very low photon flux densities. Microaglae lives in aquatic environments where light is attenuated exponentially with depth

Table 1
Distribution of some of microalgae main pigments (+ contains, − lack) [53].

Algae group	Chlorophyll						*Carotenoids*	Phycobilins	Phycocyanin
	a	*b*	c_1	c_2	c_3	*d*			
Chlorophyta	+	+	−	−	−	−	+	−	−
Euglenophyta	+	+	−	−	−	−	−	−	−
Heterokontophyta	+	−	+/−	+/−	−/+	−	+/−	−	−
Haptophyta	+	−	+/−	+	+/−	−	−	−	−
Dinophyta	+	−	−/+	+	−	−	+	−	−
Phaeophyta	+	−	+	+	−	−	−	−	−
Cryptophyta	+	−	−	−	−	−	−	+	+
Rhodophyta	+	−	−	−	−	−	−	+	+
Cyanophyta	+	−	−	−	−	−/+	−	+	+
Prochlorophyta	+	+	−	−	−	−	−	−	−

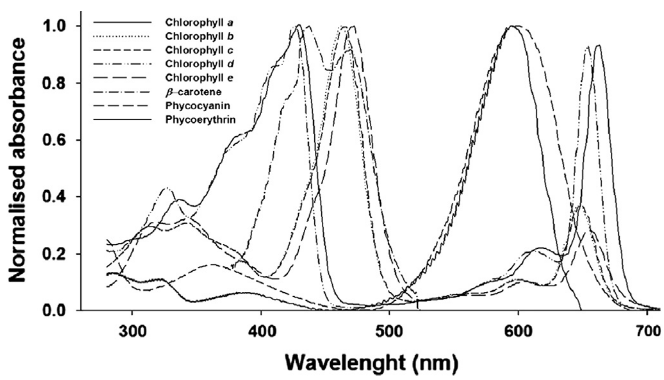

Fig. 3. Normalised absorbance spectra of some photosynthetic pigments.

Table 2
Power output from various solar cell technologies where parts of the spectrum are used by chlorophyll and pigments.

Power (w/m^2)	Chl *a*	Chl *b*	Chl *a* & Chl *b*	Chl *a* & Chl *c*	Chl *a* & Chl *b* and β-carotene	Diatoms & haptophytes
Crystalline silicon solar cell	164	172	148	164	144	112
Amorphous silicon solar cell	55	59	44	55	41	16.5
Micromorph tandem cell	76	81	65	76	63	40.3

according to Lambert–Beer Law. In addition to attenuating light, water selectively filters the light passing through it and the quality of light penetrating to depth varies in different water types [50]. As a matter of fact, the downward irradiance diminishes in an approximately exponential manner with depth. Essentially all the light absorption that takes place in algae culture is attributed to (a) the water itself, (b) photosynthetic biota and (c) any inanimate particulate matter. There are only two things that can happen to light within water: (a) it can be absorbed or (b) it can be scattered. The absorption and scattering properties of the aquatic medium for light are specific in terms of: (a) absorption coefficient, (b) scattering coefficient and (c) the volume of scattering function [51]. In the process of photosynthesis, light is captured by photosynthetic pigments that use the absorbed energy to generate reducing power in the form of $NADPH_2$ and biochemical in the form of ATP and the enzymes that use the $NADPH_2$ and the ATP to convert the CO_2 and water to carbohydrate. In eukaryotes, the pigments and electron carriers are based on thylakoid and the enzymes of CO_2 fixation are distributed throughout the chloroplast stroma. Chloroplasts occupy a substantial part of the cytoplasmic volume to ensure that most of the light incident on the cell passes through chloroplasts. In microalgae, chloroplasts can occur singly, in pairs, four or more. The task of accumulating light energy is carried out by photosynthetic pigments. These pigments are capable of absorbing light in different parts of 400–700 nm range (PAR). There are three chemically distinct types of photosynthetic pigments: (a) the chlorophylls, (b) the carotenoids and (c) the biliproteins. Chlorophyll a is the main photosynthetic pigments and therefore all photosynthetic organisms contain chlorophyll *a*. Other Chlorophylls are accessory pigments and which are species specific (Table 1). The main spectral absorption peaks for Chlorophylls a, b, and c is shown in Fig. 3 [52].

Carotenoids are another class of accessory photosynthetic pigment, which extend absorption still farther into the shorter wavelength end of spectrum. In green microaglae rely mostly on chlorophyll *a* and *b* for light harvesting. Other classes of microalgae, except the billiprotein containing microglae (only found in Rhodophycea, Cryptophycea and Cyanophycea), depend to a higher degree on their carotenoids to capture light. For instance, the molar ratio of carotenoid to chlorophyll *a* and *c* in Bacillariophycae, Dinophycea, and Hoptophycea are 1:0.5, 1:1.4 and 1:2, respectively [53]. In summary, the absorbance spectrum of the chloroplast thylakoid is determined by the particular kind and quantity of Chlorophyll/carotenoid and billiprotein complexes present within or attached to the membrane (Fig. 3). On the other hand, the in vivo microalgae absorbance spectrum can also be determined by the size and shape of the chloroplasts, cells and also colonies (aggregates, clumps). Therefore, it is very much possible that two species of microalgae with the same array of protein pigments and the same absorbance spectrum at the thylokoid level may have completely different in vivo absorbance spectrum in the suspensions of cells or colonies at the same pigment concentration. After all, the rate of microalgal photosynthesis depends on the rate of quanta capture from the light field which is determined by: (a) the light absorption properties of microalgae biomass and (b) the intensity and spectral quality of the light field. However, the rate of photosynthesis is not simply proportional to the rate of captured photons. The efficiency of photosynthesis, therefore, varies from one microalga to another and photosynthetic biomass productivity can be summarised by the equation: $P_b = L_i \times PE \times R_l$ where P_b is net photosynthetic biomass productivity, L_i is intercepted photosynthetic active radiation light and R_l is the amount of biomass loss due to respiration loss.

3. Use of solar spectrum to produce electricity

The use of photovoltaics, or solar cells, has been described as the ‘art of converting sunlight directly into electricity’ by using incident illumination and supplying electrons to an external circuit [4]. There are a number of different ways to produce solar cells and

a range of materials from which they can be produced. Silicon is a commonly used semiconductor material for producing solid state solar cells but there is increasing interest in other technologies, many of which have been commercialised and are in production with various materials used to produce them.

The first solar cell had a limited efficiency of 6% and was crystalline silicon based [54], as have been the majority in more recent times. However, new solar cells have designed and tested since then and are now appearing with efficiencies of more than 25% and 22% in small laboratory and full modules, respectively [55,56]. In the marketplace there are several types of solar cell technologies available including crystalline, micro-crystalline and amorphous silicon. Due to their higher efficiencies and the economies of scale, the world market is currently dominated by crystalline silicon solar cells which held over 93.5% in 2005 [57], decreasing to 83% in 2010 [58] and 86% in 2011 [59].

3.1. The semiconductor band-gap

The semiconductor band-gap, also known as the optical-gap, energy-gap or mobility-gap, is an important property of semiconductors that determines the optoelectronic properties of devices created from such semiconductors. The band-gap is the minimum amount of energy needed for an electron to jump from the valence band to the conduction band.

The value of the band-gap energy (E_g) is characteristic for each semiconductor and it affects the properties of solar cells produced from them [60]. For example, semiconductors are effectively transparent to photons of energy less than the band-gap energy as these photons have insufficient energy to excite an electron from the valence to the conduction band and hence are not absorbed.

The minimum room temperature band-gap energy values for some common semiconductors are 1.12 eV for silicon [61], 0.67 eV for germanium [61] and 1.35 eV for gallium arsenide [61]. For photovoltaic devices, the band-gap energy needs to be close to the peak of the energy range of visible light (1–3 eV) or the AM1.5 spectrum and not all semiconductors are suitable for use as solar cells, the most suitable band-gap for which is about 1–1.6 eV [4]. Although photovoltaic devices would work with a higher efficiency if they only had to absorb monochromatic light [62], normally photovoltaic devices are designed to absorb as much of the solar spectrum as possible. The response to different components of the solar spectrum can be measured using the spectral response technique.

The spectral response of a solar cell is usually defined as the output current under short-circuit conditions per unit power of incident monochromatic light as a function of wavelength [63]. The spectral response can show how well the cell could perform in the field under certain conditions; Ruther et al. have shown that amorphous silicon solar cells are more suitable for “blue” spectra while crystalline cells are more suitable for “red” spectra [64]. As such a-Si:H cells perform better in summer months while c-Si cells perform better in winter months, due to the different solar spectrum [64]. So by comparing the spectral response data to the intended operational light spectra the appropriate cell can be chosen for a given situation.

The use of the solar spectrum can also be tailored by using more sophisticated techniques such as multi-photon transitions and hot carrier extraction. Multi-photon transitions aids in the absorption of photons with energy below the band gap of the semiconductors, whereas the hot carrier extraction tends to aid in the capture of photons with energies above the bandgap.

It has been observed by Longeaud that after a period of light-soaking, the band-gap of amorphous silicon semiconductors changes by a broadening of the conduction band tail into the band-gap [65]. It was also observed that light-soaking causes the creation of states within the band-gap directly above the valence band tail [66]. The introduction of these states allows the absorption of photons which would otherwise be less than the energy of the band-gap and also allows the possibility of multi-photon transitions.

Energy is lost from photons with energies above the band gap in solar cells as heat. These hot carriers represent an area for improved efficiency in solar cell design. If they can be harvested there could be an appreciable gain in efficiency of thin film photovoltaic devices of potentially up to 21% [67]. There is evidence for hot carrier extraction in ultra thin amorphous PV using very thin semiconductor layers resulting in higher voltages and currents in blue end of the spectrum but with a lower overall efficiency due to the much thinner film [67]. The solar cell was too thin to absorb sufficient light although Kempa et al. claim a 3% efficiency. They suggest this could be overcome by using a cell with a longer optical path length to increase absorption, while maintaining a very thin film and small electrical path length.

3.2. Crystalline solar cells

Traditionally most solar cells have been made from doped crystalline semiconductors, such as crystalline silicon (c-Si). Current state of the art single crystal silicon solar cells are reaching 24.7 conversion efficiency [56]. A similar style 24% efficient (measured under AM1.5 at 25 °C) Passivated Emitter, Rear Locally-diffused (PERL) solar cell has an energy conversion efficiency of up to 46.3% under monochromatic light of 1040 nm [68]. The broad spectral response of this solar cell can be seen in Fig. 4.

3.3. Thin film solar cells

Thin film solar cells use significantly less material than bulk crystalline solar cells. This can make them more efficient in terms of the use of materials. They often consist of several thin layers of doped semiconducting material joined together as a charge separating junction (p–i–n) [60]. Thin film solar cells can be produced as semitransparent materials on glass substrates to allow illumination to pass through [69]. For more efficient solar cells several p–i–n junctions can be stacked together to create multi-junction cells which capture a greater amount of the light incident upon the cell [69]. These junctions can be identical but are more often tuned to be responsive to slightly different wavelengths of light in order to absorb as much of the solar spectrum as possible. There are many types and variations of thin film solar cells of which a small selection is listed below.

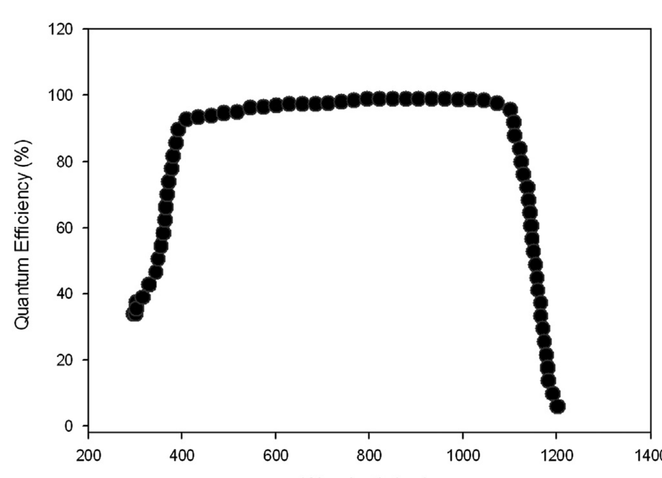

Fig. 4. Quantum efficiencies of a PERL cell [68].

3.4. Amorphous silicon solar cells

Single junction amorphous silicon solar cells have been produced with a 9.47% stabilised efficiency with much higher efficiencies produced in the laboratory [70]. Hydrogenated amorphous silicon solar cells have been in development since the late 1970s [71]. A major drawback with the use of amorphous silicon to produce thin-film solar cells is the degradation of the cell′s performance after exposure to light (photodegradation). This degradation occurs over a period of exposure to light during which the photoconductivity decreases asymptotically to a minimum point at which the cell stabilizes and further exposure to light has minimal effect. The photodegradation can be reversed by thermal annealing of the cell above 150 °C [72].

High efficiency single junction amorphous silicon devices deposited on anti-reflection coated ZnO glass substrates have been produced with a stable efficiency of 9.47% [73]. As can be seen in Fig. 5, amorphous silicon quantum efficiency is lower than that of the PERL solar cell (Fig. 4) and does not extend as far into the infrared part of the spectrum.

3.5. Microcrystalline solar cells

Microcrystalline silicon solar cells have been created with efficiencies of up to 8.9% using a single p–i–n junction [74] and 9% for substrate-n–i–p devices [75]. Microcrystalline solar cells are generally created by hot wire chemical vapour deposition (HWCVD) and combine some of the benefits of crystalline and amorphous solar cells. They are much cheaper to make than crystalline cells and they can be used on large areas. They also do not suffer from photodegradation to the same extent as amorphous solar cells. For these reasons, the use of microcrystalline silicon to produce low cost solar cells, it is growing [76].

Thin film solar cells can be stacked to produce multilayered devices with a better overall response. For example, an amorphous silicon cell can be combined with a microcrystalline cell to produce the so called ‘micromorph’ tandem solar cells [70,75,77,78]. Devices of this design have been reported with efficiencies of 12% [77]. This device design combines the benefits of microcrystalline and amorphous silicon to create a device with a high efficiency.

The tandem solar cell can take advantage of the higher quantum efficiencies of each of its components in different parts of the spectrum. The example in Fig. 6 shows the quantum efficiencies of an amorphous silicon top layer and microcrystalline silicon bottom layer [73]. By combining the two it extends the quantum efficiency of the thin film device as shown by summing the two components optimising for different parts of the solar spectrum resulting in potential improvement of the overall efficiency of a solar cell.

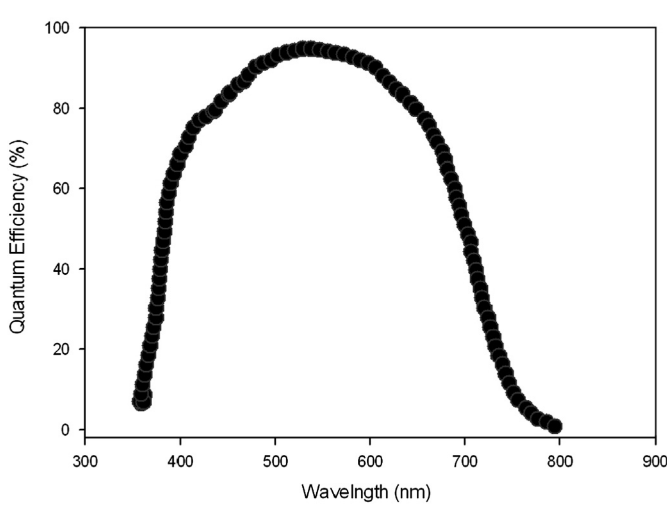

Fig. 5. Quantum efficiency of a single junction amorphous silicon solar cell after light soaking [73].

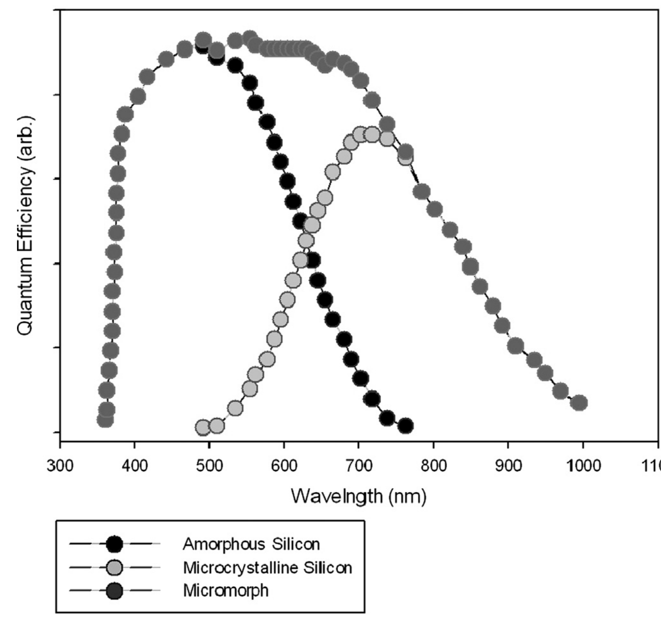

Fig. 6. Qunatum effiicencies of an amorphous silicon top and microcrystalline bottum cell [73] and combined total quantum efficiency.

3.6. Luminescent solar concentrators

Luminescent solar concentrators (LSC) can be used to increase the intensity of light incident upon a photovoltaic device from a large flat panel concentrator. These concentrators are usually formed from thin transparent polymer sheets doped with a luminescent material [62]. These flat sheet concentrators work by accepting AM1.5 through the surface of the sheet and directing a portion of this light towards the edges. Any photons with enough energy to excite the luminescent materials will do so. The luminescent material then emits a photon with a red shifted wavelength which can be trapped within the sheet by total internal reflection and directed towards the edges of the sheet where it can be collected by a solar cell [62]. The reemitted photon by the luminescent material tends to be emitted in a random direction. Although some photons are transmitted out of the LSC, a certain portion of the emitted photons will be trapped by total internal reflection within the thin layers of the LSC.

Photons with insufficient energy to excite the luminescent material would pass through the transparent sheets unaffected. As shown in Fig. 7, some photons are also lost from the LSC after the re-emission from the luminescent material.

Although the efficiency of LSC have historically been fairly low [62], there have been devices reported with efficiencies of up to 7.1% [62] which bodes well for the technology. This style of solar concentrator combined with a photovoltaic device that absorbs strongly in one part of the solar spectrum could allow for the efficient use of the solar spectrum where part is diverted from electricity generation to the growth of microalgae.

As mentioned earlier, only certain parts of the solar spectrum are required for algae growth. The main focus here is to capture the reminder of the spectrum using a LSC or a combination of technologies, for electricity production (Fig. 7) allowing the rest of the spectrum to be absorbed by the microalgae culture. Below is a

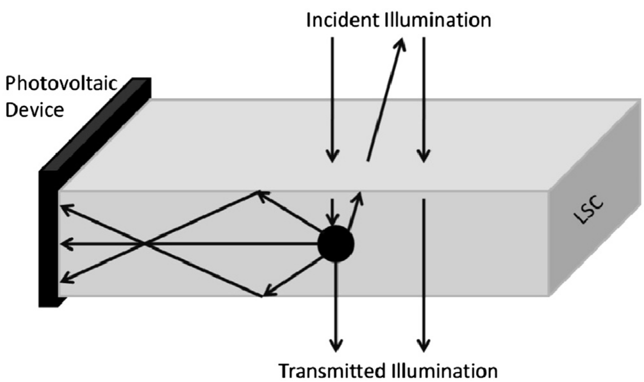

Fig. 7. 3D schematic view of a LSC. Some light enters the LSC and encounters luminescent material. This is reemited and either caught by total internal reflection or lost from the LSC (after [62]).

summary of different types of current microalgae cultivation systems to which such a technology can be applied.

4. Microalgal cultivation systems

In general there are two different types of microalgal cultivation systems, open ponds and closed photobioreactors.

4.1. Open ponds

These are the most widely used systems for large-scale outdoor microalgae cultivation and most commercial microalgal cultivation is presently carried out, with few exceptions, in open systems [79]. Open systems are easier to build and operate and are more durable when compared to closed photobioreactors making them more economical. There are many types of open cultivation systems for microalgae cultivation which vary in (1) size, (2) shape, (3) material used for construction, (4) type of agitation, and (5) inclination [27,79].

However, to date only a few species of microalgae (e.g. *D. salina*, *Spirulina sp.*, *Chlorella sp.*) have been found to be able to be grown successfully at a commercial scale in open ponds [80,81]. Profitable production of microalgae, at present, is limited to comparatively few production plants producing high value health foods, most of which are located in south east Asia, Australia, and the USA [82–84]. Production costs are high, estimated to be 10–20 US $ Kg^{-1} for *Chlorella sp.* in Japan [85,86], 4–5 US$ Kg^{-1} for *Spirulina* [87–89], and between 7 and 10 US$ Kg^{-1} for *Dunaliella salina* [82,86].

Many different designs have been suggested for pond construction but only four major pond design have been developed and operated at a large-scale: (1) unstirred ponds (lakes and natural ponds), (2) inclined ponds, (3) central pivot ponds, and (4) raceway ponds [79]. Unstirred ponds represent the most economical and least technical of all commercial culture methods and are being used commercially for a number of microalgal species such as *Dunaliella salina* [18]. These type of ponds are used for culturing *D. salina* for ß-carotene production in Western Australia and South Australia [19,90]. In inclined ponds the culture suspension flows from the top to the bottom of a sloping surface and the needs to be pumped to the top of the slope [36]. High productivity has been achieved in these systems. For example, *Chlorella* production of up to 25 g m^{-2} d^{-1} was reported for a whole year in Western Australia in a 0.5 ha sloping pond [20]. Inclined ponds also have been widely used in the Czech Republic for growing *Spirulina platensis*, *Chlorella sp.* and *Scenedesmus sp.* with average productivities of 18–25 g m^{-2} d^{-1} [91]. The main advantages of inclined ponds are (1) the high turbulent flow achievable in inclined ponds together with low culture depth (less than 1 cm) results in a high cell concentration of up to 10 g L^{-1} and (2) a high surface to volume ratio when compared to other open ponds [79]. The main disadvantages of inclined ponds are (1) sedimentation of cells at points of lower turbulence resulting in cell loss and increased risk of contamination, (2) strong evaporative loss and high rates of CO_2 desorption and (3) high cost of continuously pumping culture to the head of inclined surface [79]. The productivity achieved in inclined ponds is comparable and higher with that of other open cultivation systems such as raceway pond, but with high cost of operation together with, maintenance and construction has made these types of cultivation systems not to be feasible commercially at present for microalgae species other than *Chlorella sp.* [27]. Circular cultivation (central pivot) ponds have primarily been used for large-scale cultivation of microalgae especially in South East Asia for the culture of *Chlorella sp.* [92]. Circular ponds with a centrally pivoted agitator are the oldest large-scale algae culture systems and have also been used widely for wastewater treatment [93–95].

The most common commercial microalgal culture system in use today is the paddlewheel driven raceway pond [27,79,93,96]. Raceway ponds are usually constructed in either singles or as groups of channels built by joining individual raceways together. Raceway ponds are shallow, between 15 and 25 cm in depth, constructed in a loop and normally cover an area of approximately 0.5–0.6 ha. There are a number of mixing systems for raceway ponds including paddlewheels, airlifts, jets and pumps [79,85]. Raceway ponds are mostly used for the commercial culturing of four species of microalgae including, *Chlorella sp.*, *Spirulina platensis*, *Haematococcus sp.* and *Dunaliella salina* [87,93].

4.2. Closed photobioreactors

Closed algal culture systems (photobioreactors) are not exposed to the atmosphere but are covered with a transparent material or contained within transparent tubing. Photobioreactors have the distinct advantage of preventing evaporation and reducing contamination when compared to open cultivation systems [10,97]. Although the ability to limit contamination is one of the major characteristics of photobioreactors, operations under completely sterile conditions is not achieved in any photobioreactors except in a few small, highly expensive designs developed for certain specialized purposes [27,97]. Closed and semi-closed photobioreactors are mainly proposed for the production of high value algal products [85]. However, to date closed photobioreactors main use is in aquaculture feed production [85,27,97]. In closed photobioreactors, the challenge to create a cultivation environment independent of the external environment is interrelated with a large rise in investment and operating costs, making this type cultivation system less economical than open systems [40,98]. Closed photobioreactors are mainly divided to (a) continuously stirred tank reactors (carboys) and bags [99] (b) tubular photobioreactor [100], (c) airlift photobioreactors [101], and (c) plate photobioreactors. Closed systems are characterised by the control of many of the environmental parameters. Culturing algae in these kinds of systems has the added benefit of reducing the contamination risks, limiting CO_2 losses, creating reproducible cultivation conditions, and flexibility in technical design [20,27,36]. A number of researchers have endeavoured to overcome a number of closed systems weaknesses by: (a) reducing the light path [40,102,103], (b) solving shear (turbulence) complexity [40,104,105], (c) reducing oxygen concentration, and (d) better and more economical temperature control systems [40,85,106–108]. A few commercial-scale plate photobioreactors have been built and operated, but most have been shut down after a short period of time

mainly for environmental reasons [27]. Currently the main disadvantages of closed systems are the high cost of construction, maintenance including, temperature control, cleaning and sterilisation, high oxygen build up and some scaling up difficulties [99]. However, if these difficulties can be overcome these controlled closed systems may allow commercial mass production of an increased number of microalgal species at a wider number of locations.

5. Proposed methodology

Sustainable alternative energy can replace some of our increasing energy need. One way to meet the need for an alternative, renewable liquid fuel is the production of bioethanol and biodiesel. Microalgae have been suggested as a raw material for bioenergy production. In general, sun light is the main source of all available energy on earth. Light is also the main element for the process of photosynthesis and is the main limiting factor for microalgae growth. Photosynthesis uses approximately 25% of the solar spectrum (mostly blue and red wavelengths); the rest is either reflected or heats up the growth media. One of the other well established methods for producing energy from sunlight is the use of photovoltaics, which has been described as the 'art of converting sunlight directly into electricity' [4]. A typical commercially available solar cell can convert roughly 20% of the solar spectrum into electricity.

The concept of combining photovoltaic modules with agricultural production is well established in the area of photovoltaic greenhouses. These are an example of Building Integrated Photovoltaic (BIPV) systems in which the solar modules are incorporated into the building itself [109]. Photovoltaic greenhouses combine photovoltaic modules into the parts of the greenhouse such that the overall reduction in PAR does not impact on the plants' growth [110]. The authors also noted that the use of semi-transparent or opaque elements on the greenhouse can reduce the PAR which can cause losses in plant production [110]. As such, these two methods of energy production would appear to compete for use of the same energy resource (sunlight) to produce either chemical or electrical energy. However, some plants such as groups of microalgae (i.e. Chlorophyta) generally only require the blue and red portions of the spectrum whereas certain types of solar cells are the most efficient in the green part of the solar spectrum but not as much in the red or blue portion of the spectrum. By using the AM1.5 direct solar spectrum as a baseline we can model the amount of energy in the incident irradiation that could be converted into electricity by a hypothetical lossless system. The proposed lossless system places a solar panel as a filter above the algae pond. This will modify the spectrum of light received by the algae and divert the parts of the spectrum not needed by the chlorophyll to generate electricity. The model does not consider the mechanism used to redirect the different parts of the solar spectrum. Instead, the model assumes all the light not needed by the chlorophyll is provided to a solar cell. The model does not take into account losses associated with transmission of light through the filter or reflections from the surfaces of the filter or solar cell. The model also disregards electrical resistance in the transmission of the generated electricity.

The graph in Fig. 8 shows the direct hypothetical solar spectrum with the portions used by an alga which contains Chlorophyll *a*, Chlorophyll *b*, phycocyanin, phycoetherin and β-carotene shown with a dark shade. It is to be noted that this combination can cover all groups of microalgae except Chlorophyll *c* containing microalgae (see Table 1). For the purpose of this study any part of the spectrum with a normalised absorbance greater than 0.2 for any of these pigments is modelled as being used entirely by the microalgae. The amount of irradiance converted into electrical

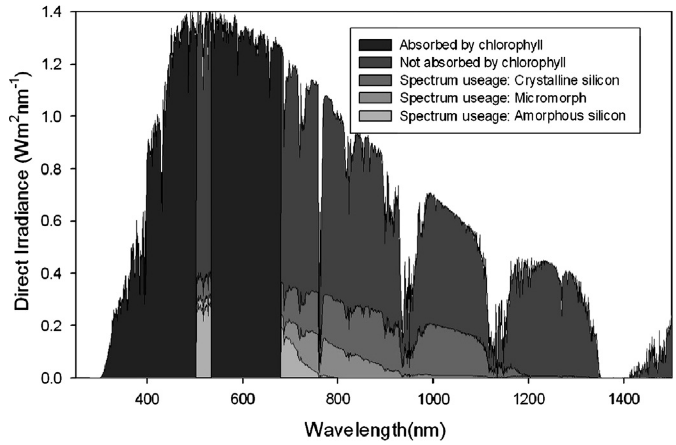

Fig. 8. Portions of the solar spectrum absorbed by green algae (Chl *a*, Chl *b*, *phycocyanin, phycoetherin and β-carotene*) and power conversion of the unused parts of the spectrum into electrical power by three types of solar cells.

energy for a hypothetical system which can deliver the regions not used by microalgae to a conventional solar cell is shown as shaded regions in the graph. The technologies, quantum efficiencies and cell efficiencies were calculated for a crystalline silicon solar cell [68], an amorphous silicon solar cell [73] and a micromorph tandem cell [73].

The amount of electrical energy produced by the three types of solar cell technologies from parts of the solar spectrum unused by microalgae can be calculated by examining the quantum efficiencies in different parts of the spectrum and the overall efficiency of the device (Table 2). These calculations indicate up to 112 W m^{-2} under AM1.5 direct solar radiation or 551–1102 MJ m^{-2} yr^{-1}, depending on location, can be generated by a highly efficient crystalline silicon solar cell if the portions of the spectrum required by green algae (blue and red portion) were diverted away from the solar cell. Assuming a photosynthetic biofuel production rate of a green alga with Chlorophylls *a* and *b* and β-carotene = 20 g m^{-2} d^{-1} [111], which is equal to around 2–8% photosynthetic efficiency [112], and a calorific energy content of 15–20 MJ Kg^{-1}, the annual production rate of algae biomass will be between 109 and 146 MJ m^{-2} yr^{-1}. By tailoring the portions of spectrum received by the microalgae this could be increased and it will be a matter of optimisation to determine which parts of the spectrum can be used for biofuel production and which for electricity generation.

The energy harvested by a highly efficient crystalline silicon solar cell could be used to add additional illumination to the algae ponds at the wavelengths needed by the microalgae. If a LED system with external quantum efficiencies in the order of 55% [113], for red wavelengths, were used, an additional 303–606 MJ m^{-2} yr^{-1}could be made available for use by the microalgae. If all of the energy was directed to highly efficient red LEDs, providing additional illumination to the microalgae, this could result in a 16.5% increase in biofuel production when compared to using the generated electricity to power other systems. This assumes no loss in energy via electrical resistance or loss in light through reflections. We assume here that all the additional energy provided to the microalgae by way of red illumination is able to be converted to biofuel. This also assumes that the productivity of the microalgae does not change when illuminated by a modified spectrum as opposed to an AM1.5 spectrum. Based on the model explained earlier, the amount of energy produced by the solar cell system (25% efficiency) would be 551–1102 MJ m^{-2} yr^{-1}. We recognise that, if the solar cells are in the order of 25% efficient, they would be producing more electrical energy per year from the spectrum they receive than the algae are storing as energy. However, the advantage of our proposed method is producing chemical energy

for transportation. While electricity can very much be used as a source of energy for electrical cars, it has its limitation such as dependence on batteries.

This suggests that a combination of the two energy production systems would allow for a full utilisation of the solar spectrum allowing both chemical energy and electricity production from the one facility making efficient use of available land, or the enhancement of bioenergy production by management of the spectrum. Therefore, we propose to introduce a solar panel as a filter above the algae pond to modify the spectrum of light received by the algae and using the unused parts of the spectrum to generate electricity. Crystalline silicon, although highly efficient is opaque and would not transit light through, rather a thin film or alternative approach may need to be considered. A carefully tailored multi-junction semi transparent thin film solar cell would allow for the absorption of different components of the solar spectrum; however they tend to absorb most photons with energy greater than the bandgap. This means a semitransparent thin film solar cell could be used to harvest the higher frequency end (blue and green) of the spectrum and allow the lower frequency (red) region to pass. This transmission of red light would be used by the chlorophyll and associated pigments. However, the blue end of the spectrum would be missing and would potentially need to be supplemented by additional illumination (as in an LED bioreactor).

Although thin film solar cells can be made semi transparent they are usually designed to absorb as much light as possible. A highly absorbent thin film device would block portions of the spectrum needed by the chlorophyll. It is also known that photovoltaic devices would work with a higher efficiency if they only had to absorb monochromatic light [62]. The use of an LSC to convert the higher frequency components of the solar spectrum through a careful choice of luminescent dyes could allow the portion of the solar spectrum needed by algae (red) to pass straight through the device. Other portions of the spectrum (blue and green) could be diverted to the generation of electricity via a high efficiency matched solar cell. Large LSC could be installed above open area algae ponds to modify and make efficient use of the solar spectrum. The needed blue portion of the spectrum can be provided by illumination powered by the electricity generated by the LSC array. The major advantage of the LSC to thin film solar cells is the cost of the material used as a filter array. One other method of diverting parts of the solar spectrum is by the use of light selective filters. A patent exists for the use of dye-sensitised solar cells incorporated into the design of greenhouses [114] that uses filters that selectively transmit light. The filter associated with these cells reflects parts of the solar spectrum back to the solar cells for efficient absorption.

Our suggested filter can alternatively be installed on raceway and inclined ponds. If filters can also take up the infra-red (heat) portion of light spectrum, there will be a significant reduction in the evaporation rate of the ponds. It is to be noted that most places with high light irradiance also have a high evaporation rate and the use of filtered light could reduce the use of freshwater in the production facility. High evaporation rate can increase the salinity and result in lowering biomass productivity. Such a filter can especially increase the performance of the inclined ponds as these ponds operate on a much lower depth (1–3 cm) compared to raceway ponds (20–30 cm). Modifying the spectrum received by the algae could aid their growth by reducing heating of growth media. Temperature also imposes critical limits on the growth of microalgae. By being able to avoid excess heating of the growth media the yield of biomass can be improved. The electricity generated by the associated photovoltaics can aid the production by powering motors and electronic systems to reduce the costs associated with production, dewatering and extraction of oil from microalgae in a remote area. The electricity can also be used augment the light received by the algae to aid their growth.

6. Conclusion

Whilst other factors can influence actual productivity, photosynthesis stipulates the potential upper limit on the effectiveness with which solar energy can be transformed into stored chemical energy (i.e. carbohydrate, lipid and protein). Therefore, photosynthesis is the ultimate source of all biomass production. Solar panels have also been recognised as a potential electrical energy production system. By combining two energy production systems one can fully utilise the solar spectrum and light incident on a surface. This would allow both the production of chemical energy (biomass) and electricity from the one facility making efficient use of available land. We propose introducing a filter or active thin film photovoltaic device above an algae pond to modify the spectrum of light received by the algae and harnessing the unused parts of the spectrum to generate electricity. For a green algae based pond this could produce as much as 112 W m^{-2}.Introducing a method of cogeneration of electrical energy has benefits in the remote areas, such as northern and central Australia, that microalgae cultivation takes place. In these areas the cogeneration of electricity reduces the reliance on grid supplied electricity and diesel generators. By generating some of its own electricity, rather than purchasing electricity (or diesel fuel), the costs associated with production, dewatering and extraction of oil from microalgae can be reduced. This allows for the cheaper and more efficient production of bioenergy or value added crops in remote locations which are located away from sources of electrical power.

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